

The University of Chicago

THE PHOTOGRAPHIC INFRARED ABSORPTION
SPECTRUM OF GASEOUS AMMONIA

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE PHYS-
ICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1935

By

SIU-HUNG CHAO

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Reprinted from
THE PHYSICAL REVIEW
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The Photographic Infrared Absorption Spectrum of Gaseous Ammonia

SIU-HUNG CHAO,* *Ryerson Physical Laboratory, University of Chicago*

(Received March 2, 1936)

The photographic infrared absorption bands of ammonia at about 10,000A, 7920A, and 6470A have been measured with greater dispersion and resolving power than hitherto. Several series have been established in the first two bands by combination principle methods, but most of the band lines have not been classified. The complexity of structure occurs probably because each observed band is a composite of several parallel-type and perpendicular-type bands; the observed series, or most of them, probably constitute parallel bands. In the pure gas, the band lines are very sensitive to pressure, and do not become at all sharp until

the latter is far below one atmosphere (cf. Fig. 1). In mixtures of ammonia and air, however, the air pressure produces very little broadening. The application of the combination principle to parallel, perpendicular, and Raman bands is discussed, taking into account the effects of unresolved but not negligible fine structure in the lines due to near-coincidence of lines of differing K values. Analysis of earlier data yields a rough value for a certain small rotational coupling coefficient and for the centrifugal deformation rotational coefficient, in the normal state of ammonia.

I. INTRODUCTION

THE absorption spectrum of the ammonia molecule, which belongs to the class of symmetrical top molecules, has been investigated in the infrared, visible and ultraviolet regions. The five bands in the photographic infrared and visible regions have been studied by the following investigators. Lueg and Hedfeld¹ reported having resolved 375 lines in the 10,230A band and 217 lines in the 8800A band, Badger and Mecke² reported 54 lines in the 7920A band and Badger³ 57 lines in the 6470A band. The 5490A band has not been resolved. Because of the complexity of the structure, only partial analyses of these bands have been made. The present work⁴ was undertaken in the hope of increasing the resolution in these bands, by using high dispersion and the special Eastman spectroscopic plates, so as to get accurately the rotational energy levels of the normal state of ammonia by a rigorous analysis according to the combination principle method, and to identify the upper vibrational levels of these bands.

In the present work, a higher resolution of these bands than previously has been attained. As an aid to the analysis, the constants of the rotational energy levels of the normal state of ammonia, found from the pure rotation band and from the Raman spectrum, were used. How-

ever, an analysis according to the combination principle method did not succeed very well. The difficulties and resulting conclusions will be stated in Section III.

II. REVIEW OF THEORETICAL CONSIDERATIONS⁵

The symmetry of ammonia is such that in equilibrium the molecule is a regular pyramid with three hydrogen atoms at the corners of an equilateral triangle. Dennison⁶ showed that there should be four fundamental vibration frequencies, two belonging to nondegenerate symmetrical modes of vibration ("parallel-type" frequencies), and two degenerate frequencies, each corresponding to an unsymmetrical pair of modes of vibration ("perpendicular-type" frequencies).

The vibration bands may be divided into two types. In the "parallel" type, the electric moment oscillates parallel to the axis of symmetry. In the "perpendicular" type, it oscillates perpendicular to the axis. In ammonia, there should be two fundamental bands of the parallel type, say ν_1 and ν_3 , and two fundamental bands of the perpendicular type, say ν_2 and ν_4 , corresponding to the four fundamental frequencies.

The ammonia molecule in its equilibrium configuration belongs to the symmetry group C_{3v} . By group theory,⁷ there exist three irreducible representations of this group, which have been called A_1 , A_2 and E . Every vibrational wave

* Now at St. John's University, Shanghai, China.

¹ P. Lueg and K. Hedfeld, *Zeits. f. Physik* **75**, 599 (1932).

² R. M. Badger and R. Mecke, *Zeits. f. physik. Chem.* **B5**, 333 (1929).

³ R. M. Badger, *Phys. Rev.* **35**, 1038 (1930).

⁴ Preliminary account, S. H. Chao, *Phys. Rev.* **48**, 569L (1935).

⁵ Cf. e.g., E. Teller, *Hand- und Jahrbuch der chemischen Physik*, Vol. 9-2 (1934).

⁶ D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

⁷ E. Wigner, *Göttinger Nachr. Math.-Phys. Klasse* (1930), p. 133; R. S. Mulliken, *Phys. Rev.* **43**, 279 (1933).

function of ammonia (neglecting the tunnel effect) must belong to one of these three representations. Of the three types, A_1 and A_2 are nondegenerate, while E is doubly degenerate. Of the four fundamental frequencies, the two nondegenerate can be shown to belong to representation A_1 and the two degenerate to representation E . Tisza⁸ showed that the n -quantum overtones of frequencies of the types A_1 and E give vibrational states as follows:

$$[A_1^n] = A_1; \\ [E^n] = \begin{cases} E & \text{when } n \text{ is } 1, \\ A_1 + E & \text{when } n \text{ is } 2, \\ A_1 + A_2 + E & \text{when } n \text{ is } 3; \text{ etc.} \end{cases} \quad (1)$$

Parallel bands can be shown to occur for transitions $A_1 \leftrightarrow A_1$, $A_2 \leftrightarrow A_2$, or $E \leftrightarrow E$, perpendicular bands for $A_1 \leftrightarrow E$, $A_2 \leftrightarrow E$, or $E \leftrightarrow E$. Since the normal state of ammonia is of type A_1 , the four fundamental bands involving the normal state are $\nu_3(||) = (A_1 \leftarrow A_1)$, $\nu_4(\perp) = (A_1 \leftarrow E)$, $\nu_1(||) = (A_1 \leftarrow A_1)$ and $\nu_2(\perp) = (A_1 \leftarrow E)$.

As a result of the tunnel effect, in which the nitrogen atom can penetrate the potential barrier in the hydrogen triangle according to the quantum mechanics, each vibrational level as above classified is really split into two, denoted by α and β (symmetrical and antisymmetrical with respect to a central plane). There are selection rules as follows: (1) for the parallel type of band, $\alpha \leftrightarrow \beta$; (2) for the perpendicular type, $\alpha \leftrightarrow \alpha$ and $\beta \leftrightarrow \beta$; (3) for the Raman spectrum, $\alpha \leftrightarrow \alpha$ and $\beta \leftrightarrow \beta$.

It is now fairly certain⁹ that the four fundamental bands of ammonia are as follows: 10.5μ , $\nu_3(||)$; 6.13μ , $\nu_4(\perp)$; 3.0μ ($\nu_1, ||$, overlapped by $\nu_2, \perp$). Calculations by J. B. Howard¹⁰ indicate that $\nu_2, \perp$ should be at about 3450 cm^{-1} . Since such a band would overlap $\nu_1, ||$ at 3.0μ , we have an explanation of the observed structure of the 3.0μ band which, although its strongest lines can be explained as $\nu_1, ||$, with center at 3335 cm^{-1} , contains also many other lines. Further, M. Migeotte¹¹ has found in ND_3 a band anal-

ogous to the 3.0μ band of NH_3 . This consists of two overlapping bands, one of parallel and one of perpendicular type, with the latter of somewhat lower frequency than the former.

The rotational energy of the symmetrical top rotator is given by

$$E_r = \frac{h^2}{8\pi^2} \left[\frac{J(J+1)}{I_A} + \left(\frac{1}{I_C} - \frac{1}{I_A} \right) K^2 \right] + \dots, \quad (2)$$

where $Jh/2\pi$ is the total angular momentum of the molecule and $Kh/2\pi$ is its component along the figure axis, I_C and I_A being the moments of inertia along and perpendicular to the symmetry axis. By substituting $B = h^2/8\pi^2 I_A$ and $\beta = (I_A/I_C) - 1$, and assuming that the molecule is also deformed on account of rotation, the rotational energy in wave numbers is

$$F(J, K) = E_r/hc = BJ(J+1) + \beta BK^2 + DJ^2(J+1)^2 + \dots, \quad (3)$$

where $K \leq J$. When the vibrational state is of a degenerate type, there is an interaction between the angular momentum vector K and the angular momentum associated with the vibration, giving rise to a correction term $\pm 2\beta' BK$ which must be added to Eq. (3).¹²

The selection rules for transitions between rotational energy levels are (1) for the parallel type of band, $\Delta J = 0, \pm 1$ and $\Delta K = 0$; (2) for the perpendicular type, $\Delta J = 0, \pm 1$ and $\Delta K = \pm 1$; and (3) for the Raman spectrum, $\Delta J = 0, \pm 1, \pm 2$ and $\Delta K = 0$.

Because of the nuclear spin of the hydrogen atoms, the quantum weights of those levels with quantum number K divisible by three (including 0) are doubled. Besides this, there is a weight factor $2J+1$ for $K=0$, $2(2J+1)$ for $K>0$.

III. SEARCH FOR ΔF 'S AND DIFFICULTIES IN ANALYSIS; NATURE OF BANDS

In order to analyze the photographic vibration-rotation bands by the combination principle method, it is desirable to know the ΔF 's of the normal state. Perhaps the most fundamental type of ΔF is the double difference between rotational energy levels of equal K , given by

¹² E. Teller and L. Tisza, *Zeits. f. Physik* **73**, 791 (1933); M. Johnson and D. M. Dennison, *Phys. Rev.* **48**, 868 (1935).

⁸ L. Tisza, *Zeits. f. Physik* **82**, 48 (1933).

⁹ The writer is greatly indebted to Professor D. M. Dennison for correspondence (also to M. Migeotte for information on ND_3) relating to this point.

¹⁰ J. B. Howard, *J. Chem. Phys.* **3**, 207 (1935); see this paper also for earlier literature.

¹¹ Private communication to Professor Mulliken.

$$\Delta_2 F_K(J) \equiv F_K(J+1) - F_K(J-1). \quad (4)$$

For ammonia these quantities can be obtained approximately from the pure rotation band and the Raman spectrum. Another type of ΔF of some importance is the single difference for fixed K , given by

$$\Delta_1 F_K(J) \equiv F_K(J+1) - F_K(J). \quad (5)$$

Still other types of ΔF 's can be given, e.g.,

$$\Delta_2 F_J(K) = F_J(K+1) - F_J(K-1), \quad (6)$$

with J fixed.

According to the combination principle,¹³ in a given vibration-rotation band, if $\Delta K=0$, the difference of the wave numbers of a P and an R line involving a common upper rotational (and vibrational) level is

$$\Delta_2 F_K''(J) = R_K(J-1) - P_K(J+1), \quad (7)$$

where $\Delta_2 F_K''(J)$ is a difference between two lower rotational energy levels. Assuming the lower rotational levels given by Eq. (3), Eq. (4) now yields

$$\Delta_2 F_K''(J) = 2(2J+1)[B'' + 2D''(J^2 + J + 1)]. \quad (8)$$

From a study of observed $\Delta_2 F_K''(J)$'s, B'' and D'' could be evaluated.

From two lines with a common lower level, one finds for the upper rotational levels

$$\Delta_2 F_K'(J) = R_K(J) - P_K(J). \quad (9)$$

In the type of band where $\Delta K=0$ and $\Delta J=0, \pm 1$ (parallel type infrared bands), each line is composed of several, usually superposed, components due to lines with the same J' and J'' but different values of K . Since $K \leq J$, the number of superposed lines depends upon the value of J . A similar superposition of components exists also for Raman bands ($\Delta K=0, \Delta J=0, \pm 1, \pm 2$).

In attempting to apply Eqs. (7)–(9) to parallel type infrared bands (which includes the "pure rotation" bands as a special case), the compositeness of the lines, just mentioned, causes difficulty. Thus the $\Delta_2 F$'s obtained by applying Eqs. (7)–(9) represent some sort of averages over several K values. These average ΔF 's for parallel bands may be called ΔF_{Pa} 's, and are defined, e.g., by

$$\begin{aligned} \Delta_2 F_{Pa}''(J) &= R_{Pa}(J-1) - P_{Pa}(J+1) \\ &= F_{Pa}(J+1) - F_{Pa}(J-1), \end{aligned} \quad (10)$$

where the symbol R_{Pa} or P_{Pa} refers to the measured frequency of a composite line.

To be sure, the quantities $R_K(J)$, $P_K(J)$, $\Delta_2 F_K(J)$ would be independent of K , and all components of a P or R line would coincide exactly, if Eqs. (3) and (8) were exact, but in practice, as we shall find, this is not quite true. The frequency which is measured for a line, corresponding evidently to the maximum of intensity of the observed composite line, obviously depends somewhat on the distribution of intensity among the different unresolved components (different K values) which make up the observed line. It is clear that, in general, any observed $\Delta_2 F_{Pa}''(J)$ value obtained from Eq. (10) should lie somewhere between the $\Delta_2 F_K(J)$ values with $K=0$ and with $K=J$. Wright and Randall¹⁴ and Barnes¹⁵ in measuring the pure rotation band of ammonia, have obtained data allowing the evaluation of $\Delta_2 F_{Pa}''(J)$'s.

A similar situation exists for Raman effect ΔF 's. In the pure rotation Raman effect, the observed Raman shifts are precisely $\Delta_1 F(J)$'s for $\Delta J = \pm 1$, and $\Delta_2 F(J)$'s for $\Delta J = \pm 2$. We may define

$$\begin{aligned} (\Delta J = \pm 1): \Delta_1 F_{Rm}(J) &= \nu_{Rm}(J)_{\Delta J=\pm 1} \\ &= F_{Rm}(J+1) - F(J), \end{aligned} \quad (11)$$

$$\begin{aligned} (\Delta J = \pm 2): \Delta_2 F_{Rm}(J) &= \nu_{Rm}(J-1)_{\Delta J=\pm 2} \\ &= F_{Rm}(J+1) - F_{Rm}(J-1). \end{aligned} \quad (12)$$

Here again each ΔF is an average over several K values. The measured ν_{Rm} depends somewhat on the intensity distribution over the different K values. This can be shown to be different for the cases $\Delta J = \pm 1$ and ± 2 in the Raman effect, while $R(J-1) - P(J+1)$ in parallel type infrared bands is still different. Hence, unless the $\Delta_1 F_K(J)$'s and $\Delta_2 F_K(J)$'s are independent of K , one should find slight discrepancies between $\Delta_2 F_{Rm}(J)$ and $\Delta_2 F_{Pa}(J)$, and between $\Delta_2 F_{Rm}(J)$ and $\Delta_1 F_{Rm}(J-1) + \Delta_1 F_{Rm}(J)$.

In the Raman spectrum of ammonia, Lewis and Houston¹⁶ found accurately not only $\Delta_2 F_{Rm}(J)$'s

¹⁴ N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).

¹⁵ R. B. Barnes, Phys. Rev. **47**, 658 (1935).

¹⁶ C. M. Lewis and W. V. Houston, Phys. Rev. **44**, 903 (1933).

¹³ Cf. e.g., W. Jevons, *Band Spectra of Diatomic Molecules* (The Physical Society, London, 1932), p. 47.

but also $\Delta_1 F_{Rm}(J)$'s. For the changes $\Delta J = \pm 2$, assuming $\Delta_2 F_{Rm}(J)$ to be given by the equation

$$\Delta_2 F_{Rm}(J) = 2(2J+1)[B_0 + 2D_0(J^2 + J + 1)], \quad (13)$$

they found $B_0 = 9.92$ and $D_0 = -0.00052$. If Eqs. (3) and (8) were exactly valid, the coefficients B_0 , D_0 thus obtained should coincide with B'' , D'' of Eqs. (3) and (8) as applied to the normal state of the molecule. However, the Raman shifts with $\Delta J = \pm 1$ calculated from these constants deviate systematically from the observed Raman shifts. The discrepancy may be accounted for in the following way.

As already noted, each line observed in the Raman spectrum is really composed of several components of differing K value, the number of which depends upon the value of J . From the formulas for calculating the theoretical intensities of the lines,¹⁶ one finds that for a given observed line with $\Delta J = \pm 1$ the intensity of the components should be highest for the higher values of K . When $\Delta J = \pm 2$, however, the intensity of the components is highest for the smaller values of K .

Now suppose a small correction in the form $\alpha K^2 J(J+1)$ is added to Eq. (3). A correction of this form is to be expected theoretically. Eq. (3) then becomes

$$F(J, K) = (B + \alpha K^2)J(J+1) + \beta BK^2 + DJ^2(J+1)^2. \quad (14)$$

When K varies from 0 to J , there is now a slight difference in frequency between the different K components of an observed line, although in practice these differences have been too small to resolve. Since the corrections are small, each observed line will correspond to the maximum intensity of the resultant of the different components. In order to determine the position of maximum intensity for this resultant, the intensity-frequency curve of each component was assumed to have a simple triangular form, whose base was made approximately twice the half-intensity breadth of the line, in such a way that the curves would overlap each other. The position of maximum intensity was then obtained by summing the individual intensities due to the different components, and should correspond to the frequency of the measured

TABLE I. Values of $\overline{K_1^2}$ and $\overline{K_2^2}$.

J	$\overline{K_1^2}(\Delta J=1)$	$\overline{K_2^2}(\Delta J=2)$	J	$\overline{K_1^2}(\Delta J=1)$	$\overline{K_2^2}(\Delta J=2)$
0	0	0	5	16.9	3.4
1	1.4	0.2	6	24.0	7.0
2	3.2	0.4	7	33.0	8.0
3	6.2	0.6	8	44.0	10.0
4	10.9	1.3	9	57.5	11.0

line in the Raman spectrum. Then the double difference for $\Delta J = 2$ is

$$\Delta_2 F_{Rm}(J) = 2(2J+1)[B'' + 2D''(J^2 + J + 1) + \alpha'' \overline{K_2^2}], \quad (15)$$

and the difference between consecutive levels for $\Delta J = 1$ is

$$\Delta_1 F_{Rm}(J) = 2(J+1)[B'' + 2D''(J+1)^2 + \alpha'' \overline{K_1^2}], \quad (16)$$

where the bars denote averages. Values of $\overline{K_1^2}$ and of $\overline{K_2^2}$ obtained according to the procedure outlined above are given in Table I.

If these values of $\overline{K_1^2}$ and $\overline{K_2^2}$ are plotted against J^2 , it is found that the $\overline{K^2}$'s are approximately proportional to J^2 , although there are some irregularities in the plot on account of doubling of the quantum weights of those levels for which K is a multiple of three (including 0). If we put $\overline{K_1^2} = cJ^2$ for $\Delta J = 1$ and $\overline{K_2^2} = dJ^2$ for $\Delta J = 2$, where c and d are constants of proportionality, the values of the constants are found to be approximately $c = 0.69$ and $d = 0.14$. Then the equations for the Raman shifts become

$$\Delta_2 F_{Rm}(J) = 2(2J+1) \times [B'' + 2D''(J^2 + J + 1) + 0.14\alpha'' J^2] \quad (17)$$

and

$$\Delta_1 F_{Rm}(J) = 2(J+1) \times [B'' + 2D''(J+1)^2 + 0.69\alpha'' J^2]. \quad (18)$$

The values of c and d being known, α'' may be calculated from the difference between the observed $\Delta_1 F_{Rm}(J)$ Raman shifts, supposed to correspond to Eq. (18), and certain pseudo values of $\Delta_1 F_{Rm}(J)$ based on the observed $\Delta_2 F_{Rm}(J)$'s and calculated as if they were related to the latter as true $\Delta_1 F_K(J)$'s would be related to true $\Delta_2 F_K(J)$'s (cf. Eqs. (4), (5)). This difference is $2(c-d)\alpha'' J^2(J+1)$. The best fit of the observed differences with this formula is obtained for $\alpha'' = 0.00154$. The probable error in this figure is, of course, relatively large. It should be men-

tioned especially that the observed differences do not fit the predicted form $CJ^2(J+1)$ very well.

By comparing Eq. (17) with the observed values of $\Delta_2 F_{Rm}(J)$ from the Raman spectrum, taking $B''=9.92$, since B'' is evidently practically the same as B_0 , D'' is found to be -0.00061 . Thus in Eqs. (14)–(18) we have, for the normal state of ammonia, $B''=9.92$, $\alpha''=0.00154$, $D''=-0.00061$. Using Eqs. (4) and (14), we get

$$\Delta_2 F_{K''}(J) = 2(2J+1) \times [9.92 - 0.00123(J^2 + J + 1) + 0.00154K^2]. \quad (19)$$

For parallel-type bands in the infrared spectrum (cf. Eq. (10)) the Eqs. (17) and (19) are replaced by

$$\Delta_2 F_{Pa''}(J) = 2(2J+1) \times [9.92 - 0.00123(J^2 + J + 1) + 0.00154bJ^2], \quad (20)$$

where bJ^2 has been put in place of $\bar{K}^2$, b being similar to d of $\Delta_2 F_{Rm}(J)$. On comparing the values calculated from Eq. (20) after omitting the last term in the bracket with those obtained from observed values of Barnes¹⁵ in the pure rotation band of ammonia, the differences should be equal to $0.00308bJ^2(2J+1)$. Using Barnes' data, the value of b is found to be 0.45 and Eq. (20) becomes of the form

$$\Delta_2 F_{Pa''}(J) = 19.838 + 39.674J - 0.00596J^2 - 0.00212J^3. \quad (21)$$

The value of b could also have been calculated from the intensity distribution of the K components in the lines of a parallel-type band, but this was not done here.

From Eqs. (19) and (21), double differences $\Delta_2 F''(J)$ have been calculated for use in comparison with experimental data below. In the second and fourth columns, values of $\Delta_2 F_{K''}(J)$ are given for $K=0$ and $K=J$; in the third column for a mean K^2 value corresponding to $\Delta_2 F_{Pa''}(J)$.

For the perpendicular type band, the J double difference in wave numbers, with constant K , should be given by Eq. (19). If J is constant, the K double difference should be

$$\Delta_2 F_{J''}(K) = \pm 4\beta'B + 4K[\beta B + 0.00154J(J+1)]. \quad (22)$$

In analyzing the photographic bands of ammonia according to the combination principle

TABLE II.

J	$K=0$	$\bar{K}^2=bJ^2$	$K=J$
1	59.50 cm ⁻¹	59.50 cm ⁻¹	59.51 cm ⁻¹
2	99.12	99.15	99.18
3	138.66	138.74	138.84
4	178.10	178.30	178.54
5	217.40	217.78	218.25
6	256.55	257.20	258.00
7	295.50	296.52	297.77
8	334.23	335.81	337.58
9	372.72	374.85	377.46
10	410.90	413.81	417.38
11	448.80	452.67	457.39

method, it was attempted to select pairs of lines with wave number differences about equal to the known double differences $\Delta_2 F_{K''}(J)$ or $\Delta_2 F_{Pa''}(J)$ of the normal state and to arrange these into series, but this procedure gave only a few good series.

Then simple types of parallel and perpendicular bands predicted by assuming the rotational constants of the upper state levels not much different from those of the normal state were compared with the observed bands. Only the 6470A band seems to follow at all the general structure of the simple perpendicular type, but detailed consideration⁴ did not confirm this structure. Then a parallel-type band with different B and β in the upper and lower states was tried¹⁷ but the general appearance of the observed bands is far different from this type.

It seems very likely⁹ that the difficulties in analyzing the bands may be explained as follows. As several authors have pointed out, the frequencies of the main photographic bands are approximately multiples of the frequency of the band at 3.0μ . For example, Adel¹⁷ gives the equation $\nu_n = 3389n - 50n^2 - 2n^3$. But if the 3.0μ band is composed of *two* overlapping fundamental bands (cf. Section II), then the bands here under consideration may involve not only harmonics of both these fundamentals, but also a variety of combination bands. Furthermore, it is to be noted that harmonics of a perpendicular-type fundamental include in general a set of several parallel and perpendicular-type bands. Thus each of the "bands" here considered may be composed really of a number of superimposed bands, some of parallel and some of perpendicular type.

¹⁷ Cf. A. Adel, Phys. Rev. **48**, 103 (1935).

For example (cf. (1) and selection rules), the 10,230A band should according to this explanation consist of three perpendicular and three parallel bands, the λ 7920 band of four parallel and five perpendicular bands, and the λ 6470 band of five parallel and seven perpendicular bands. Besides, an additional doubling may appear in each band due to the tunnel effect (α , β doubling). Only some such degree of complexity as this seems to offer a reasonable explanation of the richness and apparent irregularity of the lines in each band, and the difficulty in carrying out an analysis with the help of the combination principle.

IV. EXPERIMENTAL WORK

The five absorption bands in the long wavelength photographic region of gaseous ammonia were photographed with a 21-foot grating (Paschen mounting), the dispersion being about 2.6A per mm in the first order. A glass absorption tube, 32 mm in diameter and 4.3 m long, with plane glass windows fused on the two ends, and a 500-watt projection lamp as a source of light, were used. Eastman spectroscopic plates of the following types were used throughout the work: types *C* and *F* for 6470A and 5490A, type *R* for 7920A, types *P* and *Q* for 8800A and type *Q* for 10,230A. The spectrograms were made first with the absorption path equal to the length of the tube. Then by reflecting light through the tube with a right-angled prism, the path was increased to double the length of the tube. The time of exposure varied greatly with the type of plate and the region of the spectrum, from one-hour exposures for the second-order spectrum of the 6470A band to 85-hour exposures for the first-order spectrum of the 10,230A band. The plates were hypersensitized in an ice-cooled bath of 4 percent ammonia solution and dried before an electric fan after being washed in alcohol. The tube was filled with ammonia gas from a small tank containing pure liquid ammonia, very kindly supplied by Professor W. C. Johnson of the Department of Chemistry. Experiments were also made at the temperature of solid CO_2 (-77°C), with which the absorption tube was packed during exposure, the ammonia pressure indicated being 14 mm. Only the strong lines of the 10,230A band then appeared on the plates,

while those of the other bands were too weak to be photographed.

The ammonia absorption lines were compared with standard lines of the second and third order spectra from a 220-volt iron arc. The wave numbers in vacuum were calculated in the usual way, except that those of the lines beyond 10,000A were computed in the way indicated by Babcock¹⁸ by extending the use of Kayser's *Tabelle der Schwingungszahlen*, in the neighborhood of 10,000A. From the best spectrograms the following numbers of lines were measured: 714 lines in 10,230A, 304 lines in 7920A and 162 lines in 6470A. Absorption lines (only a few in number) due to the water vapor band, 9420A, were identified and eliminated from the 10,230A band.

Complete tables of lines in wave numbers are given in the Appendix.

V. PRESSURE BROADENING OF THE AMMONIA BAND LINES

When Badger³ employed pressures of one to five atmospheres in photographing the ammonia 6470A band, he noticed that increasing the pressure of the gas broadened the absorption lines. All the ammonia lines in the photographic region show the same effect of broadening when the pressure is varied, and all appear to show the same degree of broadening at atmospheric pressure. In order to get the best resolution of the lines, it is important to know their width under various pressures.

The accompanying spectrograms of the 7920A band (cf. Fig. 1), of which only the central portions are reproduced, show the variation of the width of the absorption lines with pressure. The lines at 750 mm pressure are about 0.55A broad and at 95 mm they become fairly sharp. They become still sharper at still lower pressures. This is shown in the 10,230A band, where at a pressure of 14 mm when the temperature of the gas is -77°C , the line widths become extremely small. The widths of the lines depend much more upon pressure of the gas than upon path length. The different absorbing lengths under the same pressure show apparently the same degree of broadening.

¹⁸ H. D. Babcock, Phys. Rev. **46**, 382 (1934).

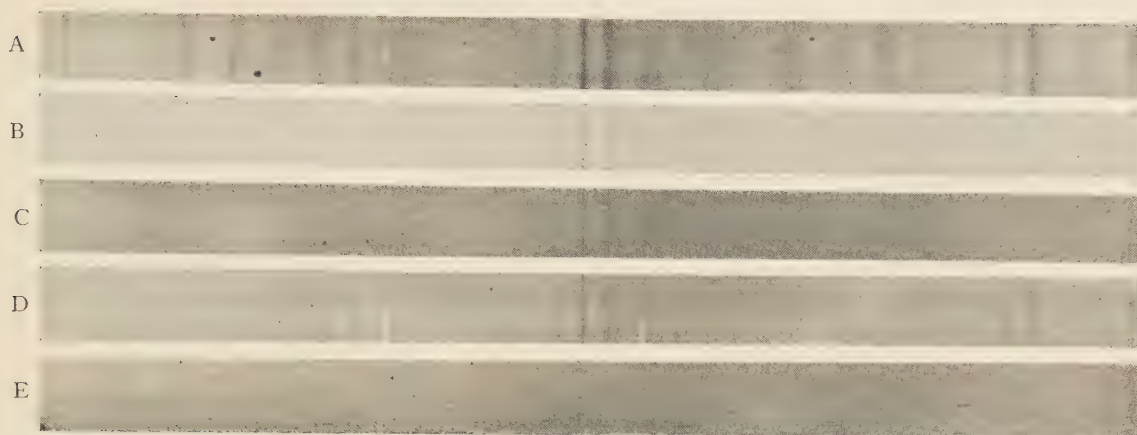


FIG. 1. 7920A band.

	A	B	C	D	E
Pressure (mm)	750	190	140	140+610 (air)	95
Absorption length (m)	4.3	8.6	8.6	8.6	4.3

The influence of a foreign gas (air) on the widths of the lines is shown in spectrogram (D), Fig. 1, for which air was admitted into the absorption tube containing ammonia at a pressure of 140 mm, making a total pressure of one atmosphere. The spectrogram of ammonia gas alone at 140 mm is also shown in (C), Fig. 1. In these two cases, the numbers of absorbing ammonia molecules are the same. Though there is a slight broadening effect of air on the absorption lines, this effect is very much smaller than that of the absorbing ammonia molecules on one another. The widths of the lines at 140 mm pressure plus 610 mm of air are shown nearly equal to those of the lines of ammonia alone at 190 mm.

In comparing the spectrogram of the ammonia lines at 750 mm pressure with that of the HCN absorption band 1.04μ at 630 mm and that of the HCl 1.20μ band, both obtained by Herzberg and Spinks,¹⁹ the widths of the ammonia lines are smaller than those of the HCN lines but are about the same as those of the HCl lines. The widths of the HCN lines are about 1.4 times those of the ammonia lines at atmospheric pressure.

In the infrared spectrum of HCl, Lasareff²⁰ and Grasse²¹ report that broadening of the ab-

sorption lines of the 3.46μ band caused by the presence of different gases is nearly the same as that caused by the absorbing gas (HCl) itself. They explained the phenomenon on the classical theory of Lorentz collision broadening. In ammonia, as well as in HCN, the pressure broadening of the lines cannot be attributed to this cause, but instead to intermolecular forces. It seems that the effect observed in ammonia may be explained in part by the intermolecular Stark effect due to the dipole moments of the molecules. Such an effect would be proportional to the dipole moment and to the number of molecules per cc.²² The dipole moment of HCN is greater than those of NH_3 and HCl, the moments being 2.5–2.6, 1.44, and 1.03×10^{-18} e.s.u., respectively.²³

An attempt has also been made to look for a dependence of the widths of the lines upon the quantum number J , but it appears that the effect, if any, must be comparatively small.

VI. FREQUENCY DATA AND ANALYSIS

10,230A AND 8800A BANDS

These two bands have been investigated by Lueg and Hedfeld,¹ but only a number of equal intervals in these bands were indicated by them. The 10,230A band appears in the present work to consist, as has not been noted previously, of

¹⁹ G. Herzberg and J. W. T. Spinks, Proc. Roy. Soc. A147, 434 (1934); Zeits. f. Physik 89, 477 (1934).

²⁰ W. Lasareff, Zeits. f. Physik 64, 598 (1930).

²¹ W. Grasse, Zeits. f. Physik 89, 261 (1934).

²² V. Weisskopf, Physik. Zeits. 34, 1 (1933). See also H. Margenau, Phys. Rev. 48, 755 (1935).

²³ Trans. Faraday Soc. 30, following p. 904 (1934).

TABLE III. Band: $\nu_0=9760.38sb$.

POSSIBLE J	POSSIBLE P BRANCH	POSSIBLE R BRANCH	POSSIBLE $\Delta_2 F''(J)$	POSSIBLE $\Delta_2 F'(J)$
0		9779.85s 9780.39s		
1	9740.31s 9741.22sb	9799.54s 9800.86m	59.58 59.13	59.23 59.64
2	9720.27m 9721.26s	9820.09s 9820.92s	99.16 99.08	99.82 99.66
3	9700.38m 9701.78m	9840.13s 9840.89w	138.69 138.59	139.75 139.11
4	9681.40s 9682.33m	9860.43w 9861.30m	178.80* 178.67*	179.03 178.97
5	9661.33sb 9662.22sb	9880.57m 9881.95w	217.67 217.59	219.24* 219.73*
6	9642.76s 9643.71m	9900.70wb 9901.64sb	256.73 256.97	257.94 257.93*
7	9623.84m 9624.98s		295.90 295.70*	
8	9604.80m 9605.89s			

two separate bands which can be distinguished by their intensity in absorption and which slightly overlap at 10,150A. The one of the longer wave-length is the stronger and its center is approximately at 10,230A. This stronger band has also been observed by Unger²⁴ using infrared technique. The center of the weaker band appears to be at 9900A.

On the high frequency side in the stronger band (10,230A), there are several groups of strong lines with intervals of about 10cm^{-1} , half the spacing characteristic of parallel-type infrared bands, suggesting a similarity to perpendicular type bands such as the 1.97μ band, studied by Stinchcomb and Barker, which also show 10cm^{-1} spacings.

The strongest 200 lines, approximately, were taken from the 10,230A band and all pairs of lines with wave-number differences about equal to the double differences $\Delta_2 F_{Pa}''(J)$ for $J=1, 2, 3$ and 4 were sorted out. For instance, taking the double difference for $J=3$ as about 138.7cm^{-1} (cf. Table II), about ten pairs of lines giving $\Delta\nu$'s agreeing with this value to within $\pm 0.05\text{cm}^{-1}$ were found. The most probable number²⁵ of accidental interval coincidences caused by random distribution of spectrum lines over 420cm^{-1} (the approximate width of the band) is about 6, thus indicating that some but not nearly all of the $\Delta\nu$'s may represent real $\Delta_2 F_{Pa}''(J)$'s. One series of close pairs of lines given in Table

TABLE IV. Band: $\nu_0=10,099.74mb$.

POSSIBLE J	POSSIBLE P BRANCH	POSSIBLE R BRANCH	POSSIBLE $\Delta_2 F''(J)$	POSSIBLE $\Delta_2 F'(J)$
0		10,119.47sb		
1	10,079.84mb	10,139.31sb	59.71	59.47
2	10,059.76mb	10,159.17w	99.62*	99.41
3	10,039.69s	10,179.01s	139.17*	139.32*
4	10,020.00s	10,198.67s	178.92	178.67
5	10,000.09s	10,218.45mb	218.43*	218.36
6	9,980.24w			

TABLE V. Band: $\nu_0=10,104.86s$.

POSSIBLE J	POSSIBLE P BRANCH	POSSIBLE R BRANCH	POSSIBLE $\Delta_2 F''(J)$	POSSIBLE $\Delta_2 F'(J)$
0		10,125.31s		
1	10,084.77m	10,145.86s	60.49*	61.09
2	64.82mb	65.71s	102.17	100.89*
3	43.69s	85.98sb	142.49	142.29
4	23.22m	10,205.89sb	183.37	182.67*
5	02.61sb	26.37m	224.70	223.76*
6	9,981.19s	47.42s	266.52	266.23
7	59.85s		307.80	
8	39.62s			

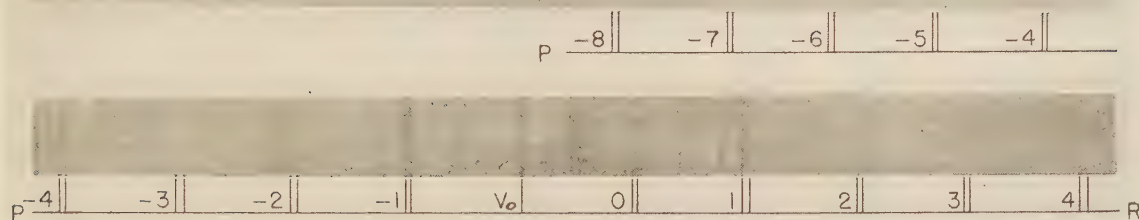
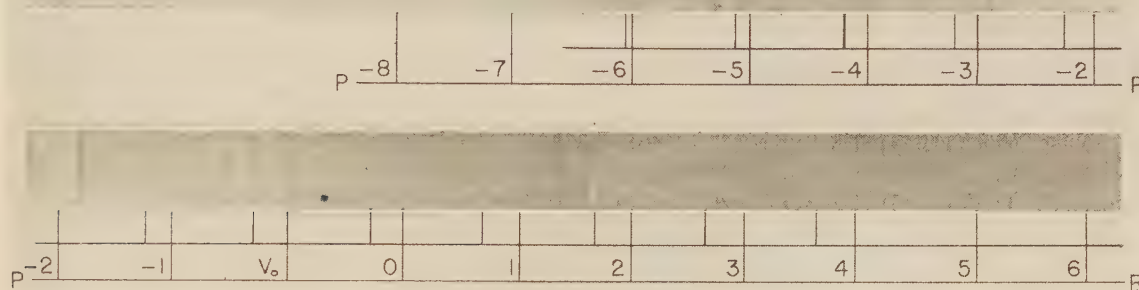
III gives $\Delta\nu$'s which agree very well with $\Delta_2 F''(J)$'s given in Table II. The lines belonging to the series form arrangements like P and R branches of a parallel band (cf. Fig. 2, where the most likely J'' values are shown, preceded by a minus sign in the case of the P branch lines). The strong line in the center of the series corresponds to the Q branch (ν_0). No other series of lines giving $\Delta\nu$'s corresponding to $\Delta_2 F'''$'s were found in the 10,230A band.

The structure of the 9900A band (cf. Fig. 3) is simpler than that of the 10,230A band. Two series of lines, given in Tables IV and V, were found in this band, one agreeing quite well with predicted $\Delta_2 F''(J)$ values given in Table II, the other not agreeing with the predicted values though it forms a good series by itself.

The doublet series with $\nu_0=9760.38$ in the 10,230A band and the series with $\nu_0=10,099.74$ in the 9900A band presumably correspond to two of the three predicted parallel bands expected near 10,000A (cf. end of Section III). The doubling in the series with $\nu_0=9760.38$ is most likely the α, β (tunnel effect) doubling. The explanation of the band with $\nu_0=10,104.86$ is not obvious; it might involve an excited lower state, but seems too strong for this; besides, no temperature-sensitiveness was observed. Perhaps the arrangement in a series is spurious.

²⁴ H. J. Unger, Phys. Rev. **43**, 123 (1933).

²⁵ G. R. Harrison, Rev. Sci. Inst. **4**, 581 (1933).

FIG. 2. 10,230A band. (v_0 should be ν_0 .)FIG. 3. 9900A band. (v_0 should be ν_0 .)

The 8800A band was also photographed but because of the rapid falling off of sensitiveness of the plate in this region, it was not used for measurement.

In the preceding tables, the small letters following the wave number of each line denote its intensity, *viz.*, *ss*=very strong, *s*=strong, *m*=medium, *w*=weak and *b*=broad. The lines in series are arranged, and *J* values assigned, so as to give double differences as close as possible to the $\Delta_2 F_{Pa}''(J)$ values from Eq. (21), but the *J* numbering might still be shifted in some cases. The broad lines are usually due to blending of two or more lines and therefore their measurements are less reliable. When differences of observed $\Delta_2 F$'s from calculated values can be explained as due to blending with other lines, or to inaccuracy of measurement due to weakness of a line, they are marked with an asterisk.

7920A BAND

Badger and Mecke² found 54 lines in this band and arranged them into several series with

a mean interval between adjacent lines equal to 19.88 cm^{-1} . They assumed the selection rule $\Delta K = \pm 1$, corresponding to the case of a perpendicular type band. Thus they took the spacing between the two strong lines in the center of the band with several lines in their neighborhood as the mean value of the coefficient of K^2 in Eq. (2), so that the moment of inertia, I_C , could apparently (but cf. Ref. 12) be evaluated.

In the present work an attempt was made to analyze the band rigorously by the combination principle method, but the structure does not fit the form either of a perpendicular type band or of a parallel type band. Two series, given in

TABLE VI. Band: $\nu_0 = 12,609.24s$.

POSSIBLE <i>J</i>	POSSIBLE <i>P</i> BRANCH	POSSIBLE <i>R</i> BRANCH	POSSIBLE $\Delta_2 F''(J)$	POSSIBLE $\Delta_2 F'(J)$
0		12,629.64s		
1	12,589.71w	49.33sb	59.73	59.62
2	69.91s	69.96s	99.07	100.05
3	50.26m	89.42s	138.73*	139.16
4	31.23w	12,708.95s	178.23	177.72
5	11.19m	29.12m	217.31*	217.93
6	12,491.64w	48.68s	257.32	257.04
7	71.80w	68.18m		296.38

TABLE VII. Band: $\nu_0 = 12,610.75s$.

POSSIBLE J	POSSIBLE P BRANCH	POSSIBLE R BRANCH	POSSIBLE $\Delta_2 F''(J)$	POSSIBLE $\Delta_2 F'(J)$
0		12,639.50s		
1	12,599.32m	58.65s	59.60	59.33
2	79.90m	79.19sb	99.20	99.29
3	59.45sb	98.37m	138.76	138.92
4	40.43m	12,718.86s	178.39	178.43
5	19.98w	37.62s	217.83	217.64
6	01.03w	56.29s	256.37	255.26
7	12,481.25w	75.71m		294.46

Tables VI and VII, were found, however. The $\Delta\nu$'s found in the two series agree with the double differences of the normal state as calculated from Eq. (21) (see Table II). The interval between the zero-lines of these two series is about 10 cm^{-1} .

It seems likely that the two series found in the 7920A band represent two of the four parallel bands expected in this region (cf. end of Section III).

6470A AND 5490A BANDS

Badger³ has investigated these two bands and found 57 lines in the 6470A band, but he indi-

cated only that the mean value of the spacing of the lines in series was 19.74 cm^{-1} . The structure of this band looks more like a perpendicular than a parallel type band. A group of strong lines which are nearly equally spaced in the center of the band suggests the Q branch of a perpendicular band, while there are also other groups of lines resembling P and R branches. However, on detailed consideration⁴ it was not found possible to reconcile the structure with that expected for either a perpendicular or a parallel band. This is not surprising in view of the considerations given at the end of Section III.

The writer wishes to express his appreciation to Professor R. S. Mulliken for the proposal of the problem and for constant inspiration and valuable advice throughout the investigation, also to Professors D. M. Dennison and E. F. Barker for helpful correspondence. He also wishes to thank Professor G. S. Monk for valuable suggestions during the work and Professor W. C. Johnson for the pure liquid ammonia.

APPENDIX

10,230A and 9900A bands

Characteristics of the line are denoted as follows: ss=very strong, s=strong, m=medium, w=weak, and b=broad.

9503.74w	14.98s	84.58w	60.76sb	11.52sb	9868.58w	42.20m	12.56sb	82.90mb	56.10w
06.67w	16.09w	9685.63s	61.71m	13.03s	69.36w	42.66m	10013.75s	83.55s	57.02m
08.29w	17.49w	86.22s	62.87w	9814.03mb	70.18s	43.46mb	14.66sb	84.77m	10158.32w
10.57w	9618.88w	87.57s	63.39s	15.30sb	71.24w	9943.99w	16.29s	85.67w	59.17w
14.17m	20.56w	88.89s	9763.94w	16.97s	72.36s	44.66m	17.20w	10086.10mb	60.31m
9518.02m	21.34m	90.04s	64.51s	17.70s	9873.28s	46.06s	17.83w	86.76m	61.64w
22.94m	22.66m	9690.24s	65.46m	18.03s	73.95s	46.49w	10018.71m	87.86w	62.32w
28.60m	23.84m	90.84w	65.83m	9818.37w	76.01s	46.95w	19.45m	89.62s	10163.09s
33.80s	9624.98s	91.33m	66.37s	19.24sb	76.91ub	9947.47w	20.00s	90.18s	64.11w
34.26w	25.93w	91.80sb	9767.04s	20.09s	77.25w	48.94w	20.84m	10090.83w	64.57w
9534.66m	27.69s	93.20m	67.73w	20.42w	9877.83w	49.33w	21.72w	91.46m	65.71s
35.09w	28.94m	9694.11m	69.18s	20.92s	78.27m	49.95w	10022.55m	92.74mb	67.16wb
35.52w	29.38m	94.84s	69.91m	9821.53s	79.09w	50.50m	23.22m	94.46mb	10168.09mb
36.29w	9630.12w	95.43s	70.70s	22.41sb	79.76m	9950.92s	23.75s	95.07s	69.30m
37.06m	30.92w	96.40m	9771.35s	23.15w	80.57m	51.66s	24.23m	10096.57mb	69.84w
9538.40m	31.97s	97.35m	72.12s	23.83s	9881.95w	52.15s	25.48mb	97.32mb	70.40w
39.20w	32.54s	9698.32m	72.67m	27.54m	82.60w	53.12m	10025.91w	98.14m	71.34w
40.65s	33.10w	700.38m	73.38s	9828.19w	83.44w	53.94w	27.11w	98.74s	10172.17w
42.84w	9635.12m	01.78m	73.93m	28.86m	85.04w	9954.49w	27.53w	99.74mb	73.04w
44.93w	35.77m	02.48m	9774.70m	29.31m	85.76w	55.01w	28.61w	10100.74s	73.61m
9546.80s	36.40mb	03.22m	75.22m	29.91sb	87.77w	55.83m	29.65w	02.56s	74.59w
47.45m	37.92w	9703.63s	75.87w	30.68s	9886.46w	56.76w	10030.88w	03.27s	75.49w
52.28s	38.53m	04.59s	76.79m	9831.32w	88.64w	58.04s	31.73m	03.91w	10176.42m
52.71w	9639.57s	05.97s	77.56mb	31.91m	89.23m	9959.13s	32.65s	04.86s	79.01s
54.23w	40.14s	07.19s	9778.85s	32.39m	89.89w	59.85s	33.23s	10105.61ub	80.72s
9554.80s	41.17m	08.39s	79.08s	33.40w	9890.71w	61.08s	34.27m	06.90s	82.11sb
55.74m	41.92s	9709.15s	79.85s	33.82m	92.44m	61.81s	10035.14m	09.50m	82.79w
56.66w	42.76s	10.68s	80.39s	9834.40w	93.08w	63.74s	36.06s	10.18m	10184.46w
57.56s	0643.71m	12.31m	81.16s	34.63w	93.56s	9965.67w	36.87m	11.76sb	85.98sb
58.41w	44.60mb	13.92s	9781.89w	35.20w	94.42w	66.71w	37.44sb	10112.33w	89.02w
9562.48s	45.09mb	16.78m	82.61m	35.77m	9895.48w	68.72w	38.63ub	13.11w	89.84w
63.65s	45.94mb	9718.26s	83.09s	36.32m	96.84mb	69.94w	10039.69s	13.74s	90.77w
64.68w	46.61mb	19.23s	83.56m	9837.22w	97.73s	71.01w	40.55m	14.76m	10192.03w
65.33m	9649.87s	20.27m	84.19w	37.74s	9872.33sb	97.73s	41.21ub	16.93s	93.51mb
67.86s	50.98s	21.26s	9784.79w	39.13s	99.86ub	73.08s	42.56wb	10117.79s	93.95w
9569.54s	52.33sb	23.89m	85.29w	40.13s	9900.70ub	73.66w	43.69s	18.57m	95.92sb
70.96s	53.11w	9724.79s	85.44w	40.89w	01.64sb	74.10w	10044.85w	19.47sb	97.63s
73.23m	54.03sb	27.36s	86.38w	9841.58w	02.99mb	75.13s	45.88s	20.35w	10198.67s
74.74s	9654.34sb	28.40s	87.01m	42.18w	03.76w	9975.86w	46.58s	20.86m	202.35s
75.23s	55.80w	29.66s	9787.92s	42.86s	04.44w	76.51m	47.63wb	10121.87m	05.89sb
9576.05w	56.60w	30.22s	88.60s	43.45s	9905.36w	77.14m	48.59wb	22.98s	07.20w
76.39m	57.43s	9734.45s	89.96s	44.11w	06.46s	79.05s	10049.52wb	23.53w	09.14m
77.67w	59.07m	35.59m	90.75s	9844.78m	08.70w	79.60w	50.61mb	24.00w	10212.64s
78.54m	9660.00w	36.00m	91.17m	45.64w	09.44w	9980.24w	52.24s	24.55m	13.42w
79.50w	61.33sb	37.07s	9791.69w	46.41m	09.94w	81.19s	54.04w	10125.31s	14.63s

10,230A and 9900A bands—Continued

9580.60s	62.22sb	38.78mb	92.11w	47.43s	9910.38m	82.76wb	54.71w	26.18s	15.43w
82.43s	64.43w	9740.31s	93.24s	49.12s	11.23mb	83.73w	10055.29w	26.82s	17.19wb
83.34s	65.12w	40.72sb	93.64m	9849.40w	12.60m	84.26w	56.10s	27.70w	10218.45mb
86.29s	9665.92s	41.22sb	94.86s	50.11s	13.47m	9984.73w	57.05w	28.38m	19.84sb
87.66s	66.29s	42.15w	9795.38w	51.03w	14.50s	85.94w	57.29w	10129.27m	20.35w
9587.99m	67.15m	42.52w	95.86m	52.13w	9915.53w	86.63s	58.38w	30.70mb	21.39w
89.42s	68.52w	9743.32m	96.55s	52.47w	17.05s	87.96w	10058.83w	32.43m	22.63mb
91.12w	69.28m	43.83m	97.00w	9853.63mb	18.97s	89.26s	59.76mb	35.39sb	10225.46wb
91.64s	9670.11s	44.81w	97.30w	54.16w	20.48w	9990.32w	60.35w	38.72sb	26.37m
93.77s	71.58w	45.39m	9797.61w	55.28m	22.03m	91.64s	61.66w	10139.31sb	27.63m
9594.84w	72.14w	46.30w	98.11w	56.36m	9923.61m	92.72m	63.21w	41.24w	28.58w
95.40w	72.98s	9747.80s	98.92w	57.44w	25.41s	93.53m	10064.82mb	41.95w	29.98w
96.10m	73.58s	48.57s	99.54s	9857.93s	26.17w	94.67m	65.95w	42.65w	10230.53s
97.64m	9674.16s	49.50m	9800.12m	58.38s	26.83w	9995.51m	67.13s	43.17w	
601.27w	74.98w	50.10w	9800.86m	59.22w	29.62s	96.34s	67.98m	10143.96s	32.50s
9603.70s	75.76s	50.70s	01.39w	59.53w	9930.93s	98.19w	68.60s	44.52s	33.57s
40.80m	76.36s	9750.95w	01.99w	60.43w	32.15w	98.99m	10069.36m	45.86s	34.11w
05.33w	76.65s	52.04m	02.96w	9861.30m	33.06w	99.63m	70.01m	46.64m	10234.60w
05.89s	9678.37s	52.66m	03.45w	61.43w	34.77m	10000.09s	71.59m	47.35m	47.42s
06.98m	78.75s	53.46s	9804.19m	62.19w	36.61sb	00.61s	73.45sb	10147.71s	48.11w
9608.38m	79.64s	54.39s	05.19m	62.84w	9937.97sb	02.61sb	74.75s	48.48w	53.14w
08.95s	80.13w	9755.53s	06.59s	63.33w	38.47w	07.06s	10077.02mb	49.02m	
09.80w	80.78s	56.61s	07.72s	9863.74s	39.09w	07.62s	78.47mb	50.23w	
11.57s	9681.40s	58.19mb	08.50w	64.19w	39.62s	10008.89s	79.84mb	51.70w	
12.32w	82.33m	59.24s	9808.66s	65.04w	40.47s	09.52sb	80.95s	10152.59sb	
9613.13w	82.95m	59.80s	09.83sb	66.10s	9941.05s	10.35s	81.44s	54.12w	
13.52m	83.91m	9760.38sb	10.56s	67.06mb	41.51w	11.13s	10082.30w	55.23m	

7920A band

12454.35w	11.19m	49.61w	83.42sb	12.27m	12637.33w	65.07w	99.52m	25.91w	64.30s
64.55w	11.82m	50.26m	85.58w	12612.81m	37.98w	66.32sb	700.86m	26.43s	12765.55m
65.93w	12.99m	51.89mb	12587.24w	13.19w	38.99s	67.85m	01.66m	12727.76s	66.22m
67.20w	14.64m	12552.92w	88.42w	13.73s	39.50s	68.74w	12702.39m	29.12m	68.18m
68.24w	12515.88m	54.49s	88.81sb	14.54m	40.76m	12669.96s	03.22w	30.48m	68.90m
12469.77mb	17.11s	54.84s	89.71w	14.94m	12641.48m	70.84m	04.04w	31.13s	71.30m
71.80w	18.48m	56.28sb	91.25w	12616.06m	42.15m	71.14m	04.61w	31.48s	12772.78m
76.71w	19.98w	58.12w	12592.01w	17.23sb	43.61s	72.22sb	05.61s	12732.78m	75.71m
77.59w	21.71sb	12558.60w	92.80m	18.48w	44.03m	12706.98w	73.72sb	33.70m	77.80m
77.98w	12522.72w	59.45sb	94.23m	19.49w	45.21s	12675.46w	07.92m	35.68m	80.06w
12479.94w	24.16m	60.75m	94.64m	19.75s	12646.32w	76.29w	08.57s	36.09s	81.15w
81.25w	25.46mb	62.18sb	95.98s	12620.72m	47.23w	77.15sb	08.95s	37.62s	12782.25m
84.41w	26.87mb	62.96w	12596.44s	21.53m	48.36w	79.19sb	10.22m	12739.15s	84.45m
84.94w	28.12w	12564.44w	97.61m	22.50w	49.33sb	81.24m	12710.78m	39.84s	88.06w
85.66w	12529.46w	66.00m	98.81m	12624.36s	50.08m	12682.07m	11.57s	40.88s	89.84w
12490.31w	30.29m	66.81w	99.32m	25.35w	12651.74mb	82.85s	12.18m	41.82m	94.43w
91.64w	31.23w	68.11w	600.08w	12626.38w	53.52w	83.76w	12.67m	44.16m	12797.47w
92.47w	33.53w	69.60s	12600.58w	12627.73s	54.29w	84.87m	13.97s	12744.92m	800.62w
93.72w	36.17mb	12569.91s	01.24w	12628.30s	55.30s	85.80m	12714.82s	45.49m	02.20w
94.88w	12537.49w	73.68w	01.54m	28.66w	55.86s	12686.89w	15.45m	46.02s	06.19w
12496.12w	38.62mb	74.78m	02.56s	29.07m	12656.52s	88.32m	16.66m	46.94s	12807.64w
97.87m	39.83w	75.82w	03.08s	12629.64s	57.23w	89.42s	17.61s	47.87s	09.46w
99.21w	40.43m	76.23w	12604.15m	30.16s	57.54w	91.50s	18.86s	12748.68s	09.63w
501.03w	41.39w	12576.89w	05.54m	31.33s	58.20w	93.20m	12719.31s	50.61s	21.77w
02.25w	12542.20sb	77.48w	06.04m	32.96s	58.65s	12694.01m	20.33m	52.46s	
12503.20w	43.96s	79.42w	07.38w	33.19s	12659.78m	95.57s	21.10m	54.46s	
04.94w	44.35s	79.90m	07.96m	12633.89m	61.28w	95.87s	22.83s	55.36s	
05.65w	44.68s	80.31m	12609.05w	34.48m	61.96w	96.43w	23.20s	12756.29s	
06.53m	46.31m	12581.56w	09.24s	35.31w	62.77s	97.06s	12723.93w	59.87m	
08.01m	12547.36w	82.12w	10.59m	36.10s	63.65s	12698.37m	24.32w	60.64m	
12509.82mb	48.36sb	82.74m	11.44w	36.58m	12663.83w	99.02m	25.29m	63.59m	

6470A band

15263.8w	29.7m	65.9m	97.2m	21.6w	15442.8m	72.3m	03.5w	29.7s	65.5w
68.6w	31.8m	15367.2w	98.2w	23.4m	44.5s	73.5w	15506.3s	30.8w	69.3w
72.3m	36.2m	68.2m	401.5w	15425.1m	46.8s	74.4m	08.2s	31.7w	15570.4w
89.4w	15339.3m	69.4w	02.8m	26.2w	47.8w	15477.8m	10.2s	32.6w	75.4w
94.6w	41.1w	70.4w	15404.4s	27.6m	48.8w	78.9m	12.5s	15533.4w	76.1w
15295.9w	42.4w	72.4w	05.5w	28.6m	15449.9s	82.4s	14.4m	34.8s	96.0w
300.2m	47.6w	15376.4s	08.2s	29.4s	50.8m	85.4m	15515.4w	35.9m	99.3w
02.2w	49.3w	78.7w	09.1w	15431.5m	52.5s	88.9s	16.5s	39.0s	15605.5w
04.2w	15351.3w	80.3s	10.0w	32.4w	53.7w	15489.9s	17.6m	41.1m	06.2w
07.5w	53.1s	83.3s	15411.1w	33.8w	55.5m	91.0w	18.9s	15543.9w	
15310.4w	54.3s	85.6m	12.2w	34.7w	15457.8m	92.0w	20.0w	45.7w	
16.4w	55.7w	15386.6w	13.9m	35.9w	58.7w	93.3s	15522.0w	48.4m	
17.2w	56.5w	87.6s	15.1m	15437.6w	59.9m	94.5w	22.7w	49.6w	
20.2w	15358.5s	90.6s	16.5w	38.1m	62.7s	15497.1s	23.9w	52.2m	
20.7w	61.9m	94.2m	15417.6m	39.4w	64.8w	99.6s	15555.3w	57.8w	
15324.3w	63.0m	95.0m	18.4w	40.2m	15466.0m	15501.5m	26.4s	59.3w	
26.4w	64.8m	15395.9w	20.0s	41.2s	66.9m	02.3w	15528.3s		

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